A Study of the Osmotic Pressure of Cane Sugar Solutions at 30°, 35° and 40°

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY WITH THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

BY

GENTRY CASH

BALTIMORE
1911

EASTON, PA.:
ESCHENBACH PRINTING CO.
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To Dr. Holland, Dr. Myers, and Mr. Carpenter the writer's thanks are due for assistance in the investigation.

PREFACE

This investigation was a study of the osmotic pressure of weight-normal solutions of cane sugar at 30° and 35°, and of ten concentrations, from 0.1 N to normal, at 40°. It is one of the series of investigations which have for their object the determination of the temperature coefficient of osmotic pressure primarily, and also the relation of osmotic pressure to concentration.

A Study of the Osmotic Pressure of Cane Sugar Solutions at 30°, 35° and 40°.

Much previous work has been done in this laboratory on the osmotic pressure of cane sugar solutions.[1] The investigations have been carried on from 0° to 25°, at intervals of 5°, with concentrations varying from 0.1 weight normal to normal. Two things, in the main, have been demonstrated: (1) that the osmotic pressure of any concentration between the temperatures mentioned above is *always greater* than the calculated theoretical gas pressure, and (2) that the ratio of osmotic to gas pressure is *constant* for a given concentration between 0° and 25°. A summary of these results is given in the table on the following page, which contains the results of 147 determinations expressed in ratios of osmotic pressure to theoretical gas pressure.

Inspection of the table shows, as stated above, that osmotic pressure is always higher than theoretical gas pressure, and also that the ratio of osmotic to gas pressure of a weight-normal solution of cane sugar for any given concentration is the same whether determined at 0°, 25°, or intervening temperatures, with the one exception of the 0.1 normal at 0°. This solution is comparatively dilute, and at this temperature it is consequently very near its freezing point. An explanation of the high ratio will probably be found in this fact when it is subjected to further study. The fact that the ratios do remain constant in this manner indicates that the osmotic pressure of cane sugar solutions follows the law of Gay-Lussac, since it increases uniformly with increase of temperature, even though it is always higher than would be expected on theoretical grounds.

[1] See references on page 14.

	0.1 N	0.2 N	0.3 N	0.4 N	0.5 N	0.6 N	0.7 N	0.8 N	0.9 N	1.0 N
0°	1.106	1.061	1.061	1.060	1.068	1.076	1.083	1.093	1.104	1.115
5°	1.082	1.063	1.058	1.059	1.067	1.074	1.084	1.093	1.102	1.115
10°	1.082	1.060	1.059	1.060	1.066	1.073	1.083	1.092	1.102	1.113
15°	1.082	1.061	1.061	1.059	1.068	1.073	1.083	1.093	1.102	1.115
20°	1.084	1.062	1.060	1.060	1.067	1.075	1.084	1.093	1.103	1.115
25°	1.084	1.059	1.060	1.059	1.065	1.071	1.083	1.093	1.102	1.113
Mean	1.083	1.061	1.060	1.060	1.067	1.074	1.083	1.093	1.103	1.114

Why the ratios should be always greater than unity is as yet not definitely known. Two possibilities have been suggested. The first, and what seems to be the most probable one, is that the departure from theoretical is due to hydration of the sugar molecules in solution. If this does take place we can easily see what the result would be with respect to the osmotic pressure of such a solution. Molecules of water becoming attached to molecules of sugar, and the resulting system acting as a physical unit in solution, would virtually withdraw water from the solution, concentrate it, so to speak, and its osmotic pressure would, of necessity, be greater than would be expected from theory. This explanation would seem to be adequate if it were not for certain facts brought out by the table above and already referred to. If the excess of osmotic over theoretical gas pressure be due to hydration and consequent concentration, one would not expect this excess to be nearly so great at 25° as at 0°. But practically no difference is seen between the two temperatures. That extent of hydration should depend on concentration is also to be expected, and the table does show such a relation, but not a uniform and regular one. It will be noticed that a curious minimum in the excess occurs in the region of the 0.3, 0.4 and 0.5 normal concentration, for which no explanation has been offered. In spite of these apparent discrepancies—apparent because the phenomena of hydration are certainly not well enough understood to make them final—hydration as an explanation is regarded as promising, all the more so now, since measurements at higher temperatures have been made. It will be taken up again when these measurements are discussed.

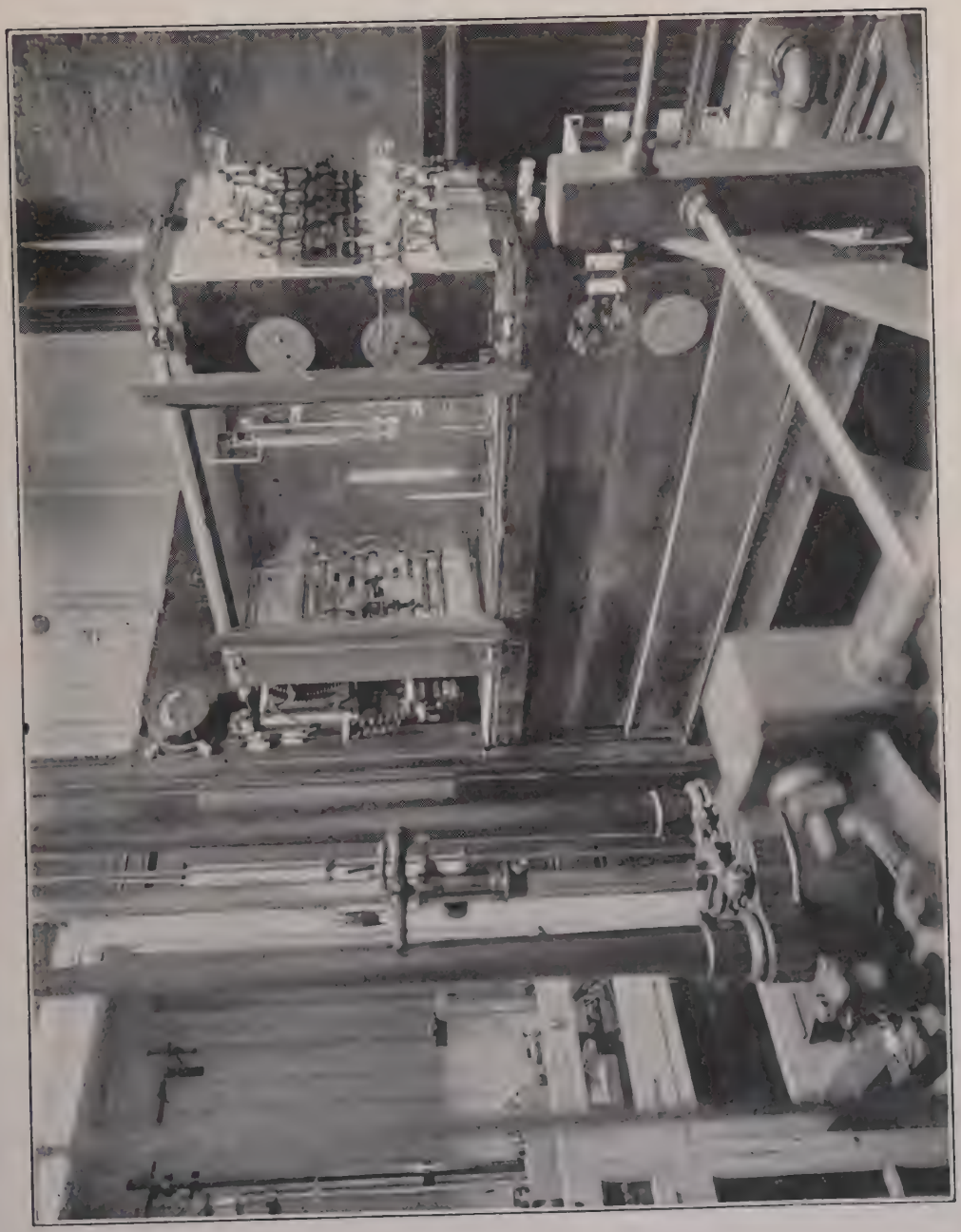
The other explanation that has been suggested for the excess of osmotic over gas pressure is the formation of water complexes, or association of water molecules. This is very similar to the hydration of a solute, and the same discussion is applicable to it. Concentration of the solvent and a diminishing of the number of particles would result, and the influence of temperature and concentration of the solute would, in general, be expected to be the same.

Last year, some preliminary measurements were made by Dr. Holland on the normal solution of cane sugar at temperatures of 30° and 40°. These temperatures were higher than any, at which determinations had ever been made before, and the work was made possible by the completion of a new osmotic pressure bath, especially designed for comparatively high temperature work. The result showed a decided departure from those obtained at 25° and under. It will be remembered that the ratio of osmotic to gas pressure for the normal solution of cane sugar at temperatures from 0° to 25° had been constant with the value 1.114. At 30° the ratio apparently dropped to 1.101. It was as though the solution had become more dilute, or, to state it in general terms, it seemed that whatever the cause for the excess of osmotic pressure over gas pressure may be, it was being *rendered less effective* by the increase of temperature from 25° to 30°, although it had *not been affected* by a change from 0° to 25°.

At 40° the same result was experienced. The ratio for the normal solution at 30° was 1.010; that at 40° was found to be 1.095. The difference between the ratio on the normal solution at 25° and below, and at 30° was 0.013; the difference between 30° and 40° was 0.006. The falling off at the ratio seemed to be *fairly regular with rise in temperature.* These results could hardly have been predicted from those that had been obtained from 0° to 25°, although we should expect something like this to take place when the possible causes for the excess of osmotic over gas pressure are considered. In this light they are highly important and interesting, and the purpose of this investigation was to repeat the work on the normal solution at 30° and 40°, measure its osmotic pressure at the intermediate temperature, 35°, and then take up the study of more dilute solutions at 40°. What the pressures of these would be at this temperature was entirely unknown.

The Bath

The bath used for these determinations was the one mentioned above as having been completed late last year. It is



not different in principle from the older baths that have been described heretofore, but is modified and improved for the maintenance of higher temperatures, from 30° to 60°. It is capable, however, of being regulated much higher. A general view is shown in Fig. 1. It is six feet long, five feet high, and 21.5 inches wide, made of heavy white pine, and is built in two sections, the upper being the "air space" and the lower the water compartment, which projects 15 inches beyond the upper, to allow the placing of the pumping mechanism. Both compartments are lined throughout with tinned copper, and are separated by a stout brass plate. This plate rests on the top of the water compartment on rubber packing. The copper cans, in which the cells and manometers are placed, extend through this plate into the water below. They are held down by lead weights attached outside the bottom, and are supported by flanged edges which also rest on rubber packing. The thermoregulators and thermometer also project into the water through holes in the brass plate, and are fixed tightly in place by means of corks. These details of construction may be seen in Fig. 2, which represents the water compartment in perspective.

From the above description it is seen that the water compartment is effectually closed, and that the "air space" above will never become saturated or ever contain an appreciable amount of water vapor no matter at what temperature the bath may be running. This is most important, since otherwise, when the insulating pads are removed from the glass doors in order to read the manometers, the cooler air outside would almost immediately cause moisture to condense on the inside of the glass, and the result would be that the readings could not be made accurately with the cathetometer, or even not at all, depending, of course, on the rapidity with which one might read, and the difference of temperature outside and inside the bath. Serious annoyance has been experienced with the older baths in this respect, even though the temperatures were comparatively low. In these baths the surface of the water was partially exposed to the air space.

The interior of the bath is reached through two doors made of heavy plate glass and opening away from each other. They comprise about two-thirds of the front side of the air space. The top is high enough to avoid the necessity of raising it, as in the older baths, when the cells are put in place in the cans.

Regulation of Temperature[1]

The principle of temperature regulation has already been stated in connection with work done in this laboratory. It is as follows: "If the water in any bath is made to pass rapidly over a continuously cooled surface, then over a heated surface which is more efficient, but which is under the control of a thermoregulator, and again over the cooling surface, etc., it should be practicable to maintain within the bath any temperature for which the thermoregulator is set; and the constancy of temperature should depend only on the sensitiveness of the thermoregulator and the rate of flow of the water."

In the bath herein described the cooling surface is the internal surface of the entire bath, since it was always kept at a temperature higher than the surrounding air. The sources of heat were of two kinds, gas and electric, the gas constant, the electric intermittent because of being controlled by the thermoregulator. Fig. 2 shows the way in which the water is circulated and heated. The propellor, run by a motor above, constantly pumps water out at 12 and 13 and back through 14 at the rate of about 350 liters a minute. The pipes 12, 13 and 14 project about 15 inches outside the bath, and are there joined by a T (see Fig. 1). Under these gas burners are placed, and they are so regulated that, although burning constantly, they will not be able to heat the water quite up to the temperature that it is desired to maintain.

The copper cans, 9 and 10, in Fig. 2, extend entirely through the bath and are open to the outside. In these the electric lamps are placed which are under the control of the

[1] Am. Chem. Jour., 45, 383.

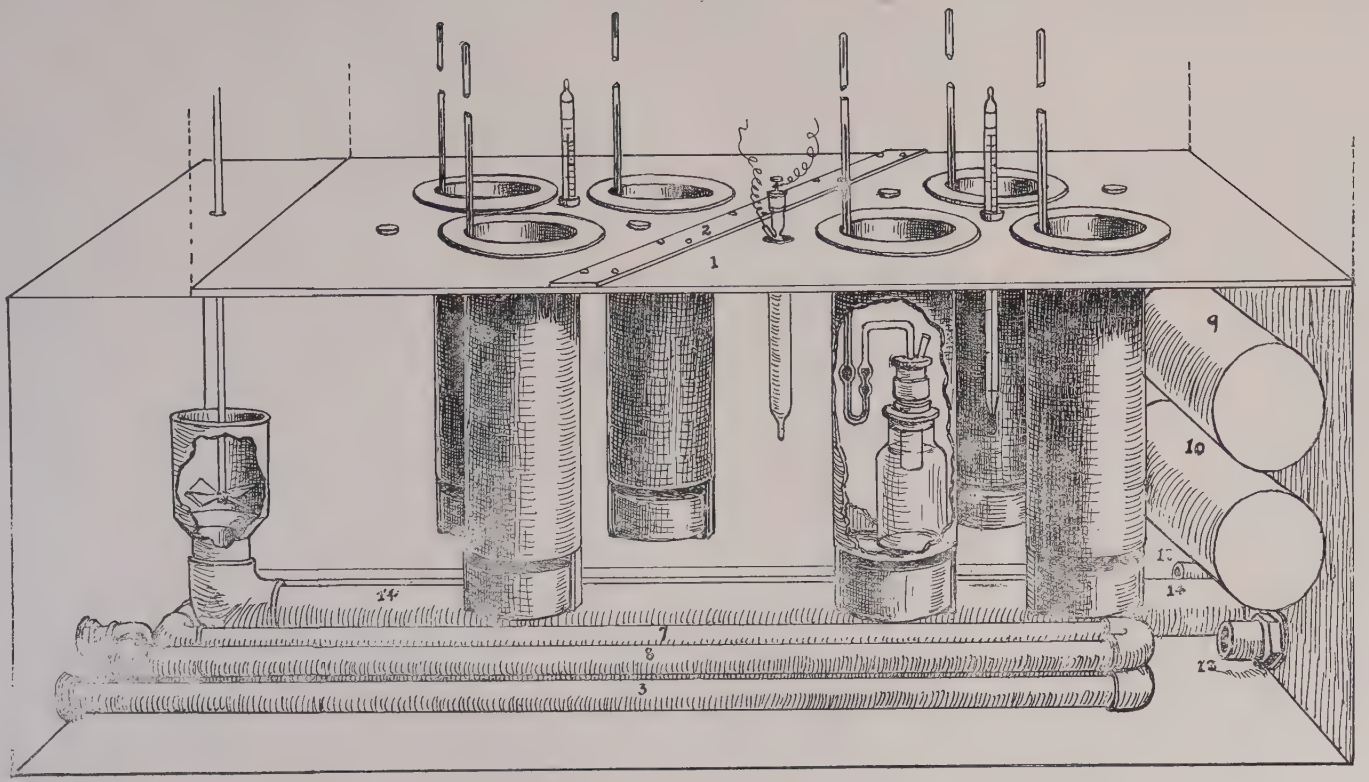


Fig. 2

thermoregulator in the water, and which serves as stove to heat the water from the temperature at which the gas burners can maintain it up to the desired point.

The air space is regulated independently of the water. The constant source of heat is the system of pipes seen in the end of the bath in Fig. 1. Water is pumped through these over burners on the outside, and back again, etc. The pump is run by a countershaft and belting from the main pump shaft in the water. This circulation of hot water is so regulated as to temperature that it will not be able to heat the air spaces quite up to the point desired. The remainder is taken care of by electric lamps placed within the air space, and under the control of the thermoregulator in the air space. The air is kept in constant circulation by means of a fan.

The thermoregulators were of large volume and consequently very sensitive. Contrary to the usual experience with the earlier arrangement, the temperature of the air was maintained almost as satisfactorily as that of the water. The contact of the platinum wire in both thermoregulators was spanned by a condenser,[1] but in spite of this the one in the water would sometimes spark. This resulted in the gradual oxidation of the mercury and consequent fouling of the capillary. Regular, but not very frequent cleansing of the capillary was necessary. The other thermoregulator worked almost perfectly throughout the whole investigation. The thermometers used were calibrated against standards from both the German Reichsanstalt and the U. S. Bureau of Standards. The one in the water was read through a compound magnifier permanently placed inside the bath. With this instrument there was very slight possibility of parallax, and the thermometer could easily be read to 0°.005. The constancy of temperature was in general very satisfactory. The maximum deviation observed for periods of seven or eight days was often more than ±0°.005. The maximum variation at other times was much greater, but in such cases was usually traceable to some definite cause, though not always. The temperature of 40° presents more difficulties

[1] Am. Chem. Jour., **45**, 383.

with respect to its regulation than do lower ones, owing to the fact that fluctuations when they do occur are more rapid and thus reach greater extent before they are detected and remedied. In the measurement recorded in the following pages no readings were recorded when the temperature was under suspicion. This may seem to be a peculiar expression when a thermometer was always in the water by which the temperature could be read, but there are grounds for it, as will be shown later when the measurements are discussed.

Connection with Previous Work

Since the object of this investigation was the determination of the temperature coefficient of the osmotic pressure of cane sugar solutions at temperatures higher than those at which all the former work had been done, and since the results obtained would be mainly of value by comparison with those that had been obtained at lower temperatures, it was necessary that the apparatus and manipulation should, as far as possible, agree with that by means of which the values at lower temperatures had been obtained. The apparatus and methods used were those that have already been described.[1] The cells were of the most recent type, and contained the copper ferrocyanide membrane.[2] It will be noticed that they are designated in two ways, all by letters, but some with sub_3 and some with sub_5. They belong to two series. The sub_3 cells are older and some have been in use for the last three years. With these same cells many of the measurements which go to form the table on page 8 were made. Cells marked with a sub_5 were "brought on" last year. They were used very little for measuring then, some of them not at all. Thus two distinct sets of cells were worked side by side and the main difference between them was in the matter of rapidity. The newer cells worked faster, and were in general more satisfactory.

When not in use, or "resting" between the times when they were set up, the cells were kept in thymol water in a large

[1] Am. Chem. Jour., **28,** 1; **36,** 1 and 39; **40,** 1, 941, 266 and 325; **41,** 1, 92 and 257.

[2] Other membranes are being tried out. See McGee's Dissertation, 1911; also Holmes' Dissertation, 1911.

desiccator which was placed in one of the baths used for membrane depositing, and described in the *American Chemical Journal* for April, 1911. This bath was regulated to the temperature at which determinations were being made, the membrane was deposited at this temperature, and in the handling of the cells they were never allowed to cool down any more than could be avoided. They were exposed to the air as little as possible, and the desiccator was carefully kept closed. These precautions were necessary to avoid infection by *penicillium* mold, which seems to feed on the nitrogen in the membrane to the great detriment of the cell, and which also seems to have become so hardy under persecution in this laboratory that ordinary fungicides have a very much diminished effect on it. The only safe way was to make extraordinary and what seemed almost excessive precautions against infection.

The manometers used were the same ones, with which the measurements at lower temperatures had been attained. All but six had not been opened or changed in any way since the measurements were made from which the table on page 8 is made up. These six were Nos. 20, 22, 2, 11, 24 and 13, and they require some discussion. The volumes of the others had been determined by the side-tube method described in the *American Chemical Journal* for May, 1908. The volumes of the six mentioned above were determined by comparison under pressure with a standard manometer. This method makes possible great range of pressures, and it was hoped that more accurate results in the determination of the *normal* volumes could be obtained by it. These manometers were found not to agree sufficiently closely with the others when used for measuring, and the method came under suspicion. Manometers whose normal volume had been determined by the side-tube method were then compared with the standard. Agreement in some cases was very good under low pressure, but "at pressures of from three to seven atmospheres a minimum in the calculated volumes was observed in all manometers compared with the standard, and at higher pressures the calculated volume steadily increased with increase of

pressure."[1] It was thought, at the time, that this discrepancy might be due to an error in the meniscus correction, as such an error would affect the calculated volume much more at high than at low pressures. This year the error was found. The meniscus correction in the standard had been applied to cubical units instead of being corrected to linear units, the system in which manometer volumes are expressed. This correction when applied to a volume curve as determined by the standard corrects the increase of the calculated normal volume, but does not straighten out the minimum in the curve.[2] This is in all probability due to a variation of capillary depression in the standard manometer. Therefore, since the object of all the present osmotic pressure work is to determine its temperature coefficient, it was deemed necessary to get all the manometers on, as nearly as possible, the same basis. Accordingly, at the beginning of this year the six manometers under question were opened, cleansed, and refilled. The volumes of the enclosed nitrogen were then determined by the side-tube method. The measurements that had been made with these manometers last year, on account of the facts mentioned above, were not regarded as trustworthy. Consequently they were repeated this year by Dr. Holland and Dr. Myers, using some of the older manometers side by side with those that had been refilled, and whose volumes had been determined this year. Agreement was satisfactory, and these results were also incorporated in the table on page 8. It would thus seem that, with respect to the manometers, the connection of this investigation with those made at lower temperatures is perfect. With one exception, all of the manometers used at the higher temperature gave consistent pressures. This exception was No. 13. The first ratios obtained with it were lower than any given by the other manometers, and, as more determinations were made, the difference seemed to be consistent. Manometers were none too plentiful, and it was thought that if this departure from the others remained

[1] Clark's Dissertation, 1910.

[2] See Carpenter's Dissertation, 1911.

the same all the time the pressures given by it could be corrected by comparison with one of the other manometers at the end of the series. However, its behavior soon became inconsistent even with its own previous performances, and it was discarded, to be used as a so-called "trial manometer," until it could be investigated. In a short time, however, a small amount of water or sugar solution appeared above the meniscus. How long this had been working over from the first bulb was not known, but it seemed very probable that the low and variable results given by the manometers were caused by the presence of water vapor in the nitrogen.

The membrane formers, that is, the potassium ferrocyanide in the sugar solution inside the cell and the solution of copper sulphate outside the cell, were of the same concentration as those that have been used in the past. Based on conductivity measurements, their concentrations are such that they are isosmotic. The question has been raised as to whether they are actually isosmotic,[1] and up to the present has not been settled. If their osmotic pressures were not equal, serious error would, of course, be introduced into a determination intended to be absolute, but since relative pressures are all that are desired at present, and since the same membrane-forming solutions have been used in all the measurements, it would seem that error from this would be limited to a change in the manner of dissociation of the potassium ferrocyanide, or a difference in the temperature coefficients of dissociation of this salt and the copper sulphate. Errors from these sources would, in all probability, however, be very small—practically negligible.

General Discussion of Measuring and Measurements

The method of setting up a cell is perhaps familiar to those who have followed the work here. Briefly it is as follows: The flask containing the sugar solution, made up by weighing, and the bottles that contain the dilute copper sulphate solution which surrounds the cells, are placed in the membrane-forming bath on a staging and allowed to come to tempera-

[1] Am. Chem. Jour., May, 1907.

ture. It will be remembered that this bath is always kept at a temperature equal to that at which the main bath is running. When the solutions have come to the temperature of the bath, the cell, which has been kept at temperature in the same bath, is rinsed at least four times with the sugar solution and filled. The brass cone, which is covered with rubber, and through which the manometer, and also a very small brass tube terminating in a larger threaded head, extend, held, in place by Wood's metal, is then pressed down into the conical neck of the cell. By means of a brass collar and nut this cone is forced down tightly into the cell. At the beginning of the tightening of the nut, the solution in the cell is forced up and out through the small tube. At what he considers the proper time the manipulator closes this opening by means of a screw plug with washer, and continues to tighten the nut. By this the mercury is forced up into the manometer tube. The point is to get the mercury to the proper height, and at the same time have the cone tight enough in the cell. The screw plug makes it possible to adjust the mercury meniscus to any point on the manometer tube, always provided the cone was not forced in too far before the cell was closed. The cell is next put into a bottle of copper sulphate solution, where it is held in place by means of a thin cork. The whole is then put back into the membrane-depositing bath where it is allowed to remain for some time and come to partial temperature equilibrium, partial because the water of the bath only comes up to the neck of the copper sulphate bottle, leaving the upper part of the cell and all of the manometer exposed to the air of the laboratory—or it may be taken immediately and placed in the main bath. Not a single case was discovered this year in which there was any leakage between the cell and the rubber on the cone. But such trouble was caused in the earlier part of the investigation by leakage about the leather washer on the plug. This was remedied by cutting out the bearing surface of the plugs very concave on the lathe and then using anti-friction rubber packing. In only four cases was there any leakage after this was done. Much annoyance was

caused throughout the entire time by leakage between the Wood's metal and the cone, the manometer tube or the small tube. These were always carefully cleaned before the metal was poured in, but the result was never certain. Sometimes cones that had been used with satisfaction for several times suddenly developed leaks, and had to be replaced. Ordinarily, however, a defect of this kind in a cone would be discovered the first time it was set up.

The height of the mercury in the manometer is adjusted as far as possible at such a point that when temperature equilibrium has been reached it will be only a little under the point of true osmotic equilibrium, so far as this point may be known. This, in the past, has presented very little difficulty at the lower temperatures, but at 30°, 35°, and especially 40°, the desired adjustment was not accomplished so easily. Although the sugar solution and cell were always at the proper temperature at the beginning of the setting up process, they necessarily cooled off more or less during this. The cell, with its liquid content, the brass collar and nut, and the manometer with its large bulbs filled with mercury, really constitute a very delicate thermometer, and the effects of temperature change on the system are best described by the term "*Thermometer effects.*" Just as soon as the cell is closed and placed in the copper sulphate solution, which, it will be remembered, is kept at temperature in the bath, the mercury in the manometer begins to rise, and when the cell is placed in the main bath, in which the entire system is enclosed, the rise is very rapid. Thus it is seen that if the mercury is adjusted to the theoretical point the establishment of temperature equilibrium will cause the pressure in the cell to run up very much too high. This is to be avoided for three reasons: (1) it is dangerous to subject the membrane to a pressure too much in excess of that which is to be measured—indeed, it is not believed that the initial mechanical pressure should ever be greater than the final osmotic pressure; (2) the solution in the cell will be concentrated by the amount of water that must be forced through the membrane before osmotic equilibrium is reached; and

(3) the time required for this, owing to the slowness of the cells, is sometimes excessively long. The proper point at which to leave the meniscus before placing the cell in the bath thus becomes a matter of importance. It depends on whether or not the cell and solution have cooled down while being set up, and this depends upon the rapidity with which the cell is filled and closed and the temperature of the laboratory. The temperature of the manometer depends upon the temperature of the laboratory also. During the earlier part of this investigation the pressure, as a rule, went too high, but as experience was gained, adjustments were more satisfactory, but never entirely so. The rule finally adopted was to leave the mercury at a point from which it would certainly not go above the point indicated by previous measurements at lower temperatures, and then complete the adjustment, if it should be necessary, after the cell had been in the main bath from 6 to 12 hours. In doing this the cell had to be taken out of the bath into the very much cooler air, and an immediate drop of the mercury was the result, which again rendered nicety of adjustment impossible. On account of the considerable number of experiments in which the pressure was high at the beginning and subsequently dropped off slowly to the point at which equilibrium was finally established, and reasoning on the basis that the hydration of the sugar molecules was the cause of a ratio of osmotic to gas pressure which had been always greater than unity, it was thought that perhaps this high initial pressure followed by a slow decrease might be caused by a slow dissociation of the sugar-water complexes under the influence of the higher temperatures. It should be stated here, in anticipation of the results of this investigation, that the ratios[1] determined were in every case lower than those obtained at temperatures of 25° or under. From a study of the measurements, however, it seems that *thermometer effects* are adequate for the explanation of this phenomenon. The way in which a cell and attached manometer acts as a thermometer

[1] $\frac{\text{Osmotic pressure}}{\text{Gas pressure}}$.

has already been referred to. Of course, if the membrane permitted the rapid passage of water through itself, changes of pressure due to changes of temperature would be as rapidly compensated. As the membrane in the cells used actually is, however, water can only pass through it very slowly, so slowly that a change of pressure due to permanent changes of temperature after the cell has been closed may be obliterated before several days. The measurements that showed this high initial pressure in the most marked degree were the lower concentrations at 40°. The high pressure was in every case reached in about 24 hours after the cell had been placed in the bath, and after it had been adjusted. From the extreme slowness of the cells it would seem impossible for this high pressure so soon after the cell had been set up to be due to osmotic pressure alone, or even in very great part. Let us consider a case more in detail. A cell has been set up and placed in the bath. After 12 hours it may be presumed that it has come to *temperature* equilibrium, then, if the pressure in the cell were not equal to the osmotic pressure of the solution which had not as yet reached disassociation equilibrium, the meniscus would rise until these became equal, and then fall, following the change in the solution, until permanent equilibrium was reached. Consequently we should expect some of the pressure curves to show a maximum. None of them, however, did so.

In addition to the high temperature as a factor in making nice adjustment difficult, it should also be mentioned that on the lower concentrations at 40° nothing was known as to what their pressures were. Such a large drop in these ratios was not anticipated, and in several cases cells that had apparently reached temperature equilibrium, but were much too low when judged by ratios at 25° or under, were tightened and the pressure increased in order to prevent dilution, and to save time. As it turned out, however, when the pressure was thought to be much too low, it was nearer correct than after it had been increased, and the result was that water was forced from the sugar solution until equilibrium was reached. This happened in some

cases in such a degree that the sugar solution was appreciably concentrated.

Perhaps the best evidence that whatever is happening in the solution to lower the ratio does not take place slowly, is the fact that in several experiments the conditions were such that almost the very first readings gave a ratio which, as the experiment was continued, proved to be the correct one.

As mentioned above, it was found in several determinations that the sugar solution had become concentrated. This was manifestly due in some cases to the too high initial pressure, caused by thermometer effects; in others it occurred when the initial pressure was never observed to be higher than the final pressure. It is not very clear just how concentration can take place in the second case. In the past, some anomalous changes of pressure have been ascribed to the slipping or moving of the adjusting collar and nut, and also to the flowing under pressure of the rubber which makes the joints between the cone and the cell. Such a flowing of the rubber would allow the cone gradually to descend farther into the cell, and the pressure inside the cell would be increased thereby. This would account for a rise of the mercury which was too rapid to be ascribed to osmotic pressure, and which took place after the cell must have reached temperature equilibrium, and in cases where the pressure was already higher than the true osmotic pressure. As has been mentioned, such increases of pressure were of common occurrence, much more so than had been experienced in work at lower temperatures. The increase in the plasticity of rubber with increase of temperature might have some bearing on the question. An example of a strange change of pressure that could be assigned to a movement on the part of some of the closing and adjusting parts will be seen in Exp. No. 14.

The comparatively long time required for the rubber to come to pressure equilibrium might also explain cases in which concentration occurred when the pressure as read and calculated was at no time greater than that finally obtained. If the rate at which the pressure was being increased

by a slow downward movement of the cone were very nearly equal to the rate at which the pressure was being diminished by the passage of water through the membrane, then a concentration of the solution would result which could not have been predicted by any observations on the meniscus. The same thing could be said of the slow increase of pressure as the cell was approaching final temperature equilibrium. Another possible cause for concentration was the exposure of the sugar solution heated to 40° to air when the cell was being rinsed and filled.

The slowness of the old cells, by which is meant the rate at which water can pass through the membrane, has already been referred to as a factor in the long time required for the attaining of equilibrium. An experiment was performed in order to test the rate at which this took place. Cell D_3 was thoroughly rinsed with a normal solution of sugar whose rotation had been determined and then filled. It was stopped up at atmospheric pressure and placed in the ordinary copper sulphate solution, everything being at temperature, and kept so. After 15 minutes the solution was taken out of the cell, cooled and read in the saccharimeter. No loss in rotation was detected. It was replaced, and read again after five hours. No loss in rotation could be found even after this long time, although there was no pressure inside the cell. Some water entered, of course, but it was not enough to be detected by the saccharimeter. The slowness of the old cells is in marked contrast to the behavior of new ones. These, when set up with trial manometers as they are being "brought on," have been known to develop in less than an hour a pressure of 25 atmospheres starting at normal atmospheric pressure.

Several times a reading of the cells in the bath was taken—usually it would be the first one in the mornings, and the readings were all found to come uniformly low, or high, although the thermometers might register the proper temperature. In such a case it was evident that the temperature had been off some time before, and that the effects still remained. This was made doubly certain by the fact that measurements that had been constant before the change

returned to their constant pressures within 10 or 12 hours usually. This was what was meant by "suspicioning the temperature," a phrase used earlier in the present writing.

The Measurements

At the beginning of the investigation it was the intention to measure only the *even* concentrations between the 0.1 N and normal, including these two. But as the work progressed the results proved so interesting that it was thought best to measure all ten concentrations. Accordingly, on the first of March, Dr. Holland and Dr. Myers also took up the work at 40°, and we put forth every effort to complete the series by the end of the scholastic year. Although at the same temperature, we worked independently so far as baths, cells, manometers, readings, calculation, and practically all details of manipulation were concerned. The measurements obtained by the writer are given in detail in the following pages, then *all* the measurements at 40° are compared and summarized. The agreement is satisfactory.

A total of about 100 experiments was set up at 40°. Of these 32 were regarded as beyond suspicion. A good percentage of the failures was due to leaks about the washer or in the cone. Most, however, were due to some fault of the cell itself, manifested by inability to attain and *hold* a constant pressure. This constant pressure was not necessarily the maximum. Some measurements were obtained in which a low pressure was maintained for days, giving a low ratio. The causes for such ratios have been previously discussed,[1] but have not yet been cleared up. It is not believed that the low ratios have a pertinent bearing on the chief osmotic problems at present, namely, the establishing of the applications of the Law of Gay-Lussac and the Law of Boyle to osmotic pressure, although they are in themselves interesting. Two facts seem to preclude the attaching of very much importance to any low ratios obtained in this investigation. One is that, although they were given abundance of time, or what at least seemed so, no two agreed on any one concentration, with one exception. The other is that

[1] See Clark's Dissertation, J. H. U., 1910.

low ratios obtained at different concentrations showed no relation to each other. For example, a ratio was obtained on the 0.6 N solution at 40° which was fairly constant at 1.045, while a little later a solution of 0.7 N concentration was set up, and it remained constant at only a little above unity. We hope to understand just why maximum pressures are not always developed when more has been learned of the membrane.

So far as is known, not a single determination was lost on account of inaccuracy of temperature regulation.

The sugar solutions were always read in the saccharimeter before and after an experiment. It has been the custom in this laboratory to reject the result given by any solution that showed a change in rotation of more than 0°.1, this being about the limit of accuracy when the solutions are darkened by the presence of potassium ferrocyanide. Practically all of the changes in concentration in the past at the lower temperatures have been *dilutions*. In the work at 40° the conditions seemed to be especially favorable to *concentration*, as has already been referred to, and determinations that were otherwise satisfactory were corrected for this.

In the experiments which follow the date is given in column 1, volume of manometer in 2, correction for meniscus in 3, final volume of nitrogen under comparison, reduced to 0° in 4, pressure of mercury and solution in 5, capillary depression in 6, barometer in terms of standard in 7, and the total pressure in 8. All pressures are in atmospheres, and all volumes are in calibration units. The osmotic pressure is obtained by subtracting the average barometer from the average total pressure. The older cells are so slow that they cannot follow rapid fluctuations of the barometer, and if such fluctuations occur, the only way to get a truly indicative measurement is to continue the experiment a rather long time, and take averages. This is mainly true of the dilute concentrations, since, as the concentration becomes more dilute, the barometer correction has a greater proportional value.

The readings are averaged by days, and the total number of readings after the pressure became constant is given.

Experiment No. 1—Temperature, 30°

Cell No. G_5. Manometer No. 15. Resistance of membrane, 150,000 ohms. Rotation of solution before experiment, 107°.3; after, 107°.3. Concentration of solution, normal. Cell set up Dec. 3, 1910.

Time	Original vol. of N_2 in manometer under standard conditions	Correction for meniscus	Final vol. of N_2 reduced to 0°	Pressure of liquids in manometer	Capillary depression	Barometer in atmospheres	Total pressure in atmospheres
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Dec. 15	506.05	0.16	18.34	0.580	0.02	0.987	28.192
Dec. 16, 10 A.M.	506.05	0.16	18.40	0.580	0.02	0.993	28.110
Dec. 16, 5 P.M.	506.05	0.16	18.39	0.580	0.02	1.009	28.120
Dec. 17, 11 A.M.	506.05	0.16	18.39	0.580	0.02	1.009	28.120
Dec. 17, 5 P.M.	506.05	0.16	18.40	0.580	0.02	1.012	28.098
Dec. 18	506.04	0.16	18.40	0.580	0.02	1.012	28.098

Time, 82 hours.
Osmotic pressure, 27.120.
Theoretical gas pressure, 24.716.
Ratio, 1.098.

The average of 3 determinations made by Dr. Holland in May, 1910, with manometer No. 9 is 1.101.
Average of all four, 1.100.
The ratio is 0.014 lower than the ratio on the same solution at 25° and below.

Experiment No. 2—Temperature, 30°

Cell No. Z_3. Manometer No. 15. Resistance of membrane, 275,000 ohms. Rotation of solution before experiment, 98°.3; after, 98°.3. Concentration of solution, 0.9 N. Cell set up Oct. 29, 1910.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Nov. 1	506.05	0.16	20.62	0.578	0.02	1.003	25.140
Nov. 2	506.05	0.16	20.53	0.578	0.02	1.998	25.242
Nov. 3	506.05	0.16	20.57	0.578	0.02	0.995	25.199
Nov. 4	Temperature off						
Nov. 5	506.05	0.16	20.56	0.578	0.02	0.994	25.215
Nov. 6	506.05	0.16	20.57	0.578	0.02	0.992	25.194
			Mean, 20.57			0.996	25.198

Time, 146 hours.
Number of readings, 10.
Osmotic pressure, 24.202.
Theoretical gas pressure, 22.244.
Ratio, 1.088.

Experiment No. 3—Temperature, 35°

Cell No. I_5. Manometer No. 11. Resistance of membrane, 125,000 ohms. Rotation of solution at beginning of experiment, 107°.35; after, 107°.35. Concentration of solution, normal. Cell set up Jan. 6, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Jan. 12	505.05	0.16	18.06	0.541	0.02	1.010	28.558
Jan. 13	505.05	0.16	18.12	0.541	0.02	1.006	28.397
Jan. 14	505.05	0.16	18.11	0.541	0.02	0.997	28.431
Jan. 15	505.05	0.16	18.12	0.541	0.02	0.994	28.412
Jan. 16	505.05	0.16	18.12	0.541	0.02	1.010	28.416
Jan. 17	505.05	0.16	18.09	0.541	0.02	1.010	28.471
Jan. 18	505.05	0.16	18.07	0.541	0.02	1.011	28.492

This table is the average of 15 readings.
Time, 168 hours.
Osmotic pressure, 27.450.
Theoretical gas pressure, 25.124.
Ratio, 1.093.

Experiment No. 4—Temperature, 35°

Cell No. P_3. Manometer No. 15. Resistance of membrane, 400,000 ohms. Rotation of solution at beginning of experiment, 107°.35; at conclusion, 107°.35. Concentration of solution, normal. Cell set up Jan. 14, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Jan. 21	506.05	0.16	18.16	0.544	0.02	0.996	28.431
Jan. 22	506.05	0.16	18.17	0.544	0.02	1.009	28.427
Jan. 23	506.05	0.16	18.18	0.544	0.02	1.016	28.402
Jan. 24	506.05	0.16	18.17	0.544	0.02	1.020	28.407
			18.17			1.010	28.417

Number of readings, 8.
Time, 95 hours.
Osmotic pressure, 27.407.
Theoretical gas pressure, 25.124.
Ratio, 1.091.

The mean of the two determinations at 35° is 1.092. This is 0.008 lower than the average of the four determinations at 30°.

Experiment No. 5—Temperature, 40°

Cell No. F_3. Manometer No. 5. Resistance of membrane, 140,000 ohms. Rotation of solution at beginning of experiment, 107°.45; at conclusion, 107°.45. Concentration of solution, normal. Cell set up Jan. 27, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Feb. 1	584.68	0.16	20.84	0.610	0.02	1.003	28.695
Feb. 2	584.68	0.16	20.93	0.610	0.02	0.993	28.562
Feb. 3	584.68	0.16	20.85	0.610	0.02	1.006	28.684
Feb. 4	584.68	0.16	20.81	0.610	0.02	0.989	28.721
Feb. 5	584.68	0.16	20.90	0.610	0.02	1.007	28.603
		Mean,	20.87			1.000	28.653

Number of readings, 8.
Time, 62 hours.
Osmotic pressure, 27,653.
Theoretical gas pressure, 25.533.
Ratio, 1.083.

Experiment No. 6—Temperature, 40°

Cell No. I_5. Manometer No. 15. Resistance of membrane, 120,000 ohms. Rotation of solution at beginning of experiment, 107°.4; at conclusion, 107°.45. Concentration of solution, normal. Cell set up Jan. 27, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Jan. 30	506.05	0.016	17.87	0.544	0.02	0.992	28.881
Jan. 31	506.05	0.016	17.88	0.544	0.02	0.999	28.859
Feb. 1	506.05	0.016	17.85	0.544	0.02	1.003	29.908
Feb. 2	506.05	0.016	17.81	0.544	0.02	0.994	28.965
Feb. 3	506.05	0.016	17.91	0.544	0.02	1.006	28.812
Feb. 4	506.05	0.016	17.88	0.544	0.02	0.991	28.860
Feb. 5	506.05	0.016	17.91	0.544	0.02	1.007	28.819
Feb. 6	506.05	0.016	17.87	0.544	0.02	1.006	28.888
Feb. 7	506.05	0.016	17.94	0.544	0.02	1.004	28.785
Feb. 8	506.05	0.016	17.95	0.544	0.02	1.005	28.750
Feb. 9	506.05	0.016	17.95	0.544	0.02	0.998	28.751
Feb. 10	506.05	0.016	17.99	0.544	0.02	1.001	28.689
Feb. 11	506.05	0.016	17.95	0.544	0.02	1.012	28.750
Feb. 12	506.05	0.016	17.93	0.544	0.02	0.997	28.791
Feb. 13	506.05	0.016	17.96	0.544	0.02	0.998	28.736
Feb. 14	506.05	0.016	17.97	0.544	0.02	1.003	28.713
		Mean,	17.86			1.001	28.810

Number of readings, 30.

Time, 380 hours.

Osmotic pressure, 27.809.

Theoretical gas pressure, 25.533.

Ratio, 1.089.

Average of the two determinations on the normal solutions at 40°, 1.086.

Average of two determinations made by Dr. Holland last year, 1.085.

Average of all 4 determinations, 1.0855, which is 0.0065 lower than the mean of the two measurements at 35°.

Experiment No. 7—Temperature, 40°

Cell No. I_5. Manometer No. 5. Resistance of membrane, 100,000 ohms. Rotation of solution before experiment. 89°.1; at conclusion, 89°.1. Concentration of solution, 0.8 N, Cell set up 3 P.M., Feb. 3, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Feb. 27	584.68	0.16	26.37	0.602	0.02	1.007	22.779
Feb. 28	584.68	0.16	26.35	0.602	0.02	1.007	22.786
Mar. 1	584.68	0.16	26.34	0.602	0.02	0.989	22.801
Mar. 2	584.68	0.16	26.36	0.602	0.02	0.990	22.778

No. of observations, 9.
Time, 75 hours.
Osmotic pressure, 21.788.
Theoretical gas pressure, 20.426.
Ratio, 1.067.

Experiment No. 8—Temperature, 40°

Cell No. F_3. Manometer No. 15. Resistance of membrane, 140,000 ohms. Rotation of solution at beginning of experiment, 89°.1; at conclusion, 89°.5. Concentration of solution, 0.8 N. Cell set up Feb. 15, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Feb. 20	506.05	0.16	22.69	0.573	0.02	0.990	22.986
Feb. 21	506.05	0.16	22.68	0.573	0.02	1.005	22.908
Feb. 22	506.05	0.16	22.69	0.573	0.02	1.000	22.900
Feb. 23	506.06	0.16	22.71	0.573	0.02	1.003	22.879
Feb. 24	506.05	0.16	22.66	0.573	0.02	0.992	22.923
		Mean,	22.69			0.998	22.899

Number of readings, 9.
Time, 96 hours.
Osmotic pressure, 21.901.
Corrected for concentration, 21.803.
Theoretical gas pressure, 20.426.
Ratio, 1.068.

Experiment No. 9—Temperature, 40°

Cell No. F_3. Manometer No. 15. Resistance of membrane, 85,000 ohms. Rotation of solution at beginning of experiment, 89°.1; at conclusion, 89°.7. Concentration of solution. 0.8 N. Cell set up Feb. 25, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Feb. 27	506.05	0.16	22.65	0.573	0.02	1.007	22.937
Feb. 28	506.05	0.16	22.68	0.573	0.02	1.007	22.908
Mar. 1	506.05	0.16	22.62	0.573	0.02	0.993	22.957
			Mean, 22.65			1.002	22.946

Number of readings, 8.
Time, 54 hours.
Osmotic pressure, 21.944.
Corrected for concentration, 21.808.
Theoretical gas pressure, 20.426.
Ratio, 1.067.

Experiment No. 10—Temperature, 40°

Cell No. I_5. Manometer No. 5. Resistance of membrane, 120,000 ohms. Rotation of solution at beginning of experiment, 48°.0; at conclusion, 48°.0. Concentration of solution, 0.4 N. Cell set up 3 P.M., March 11, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Mar. 15	584.68	0.16	53.11	0.560	0.02	0.987	11.568
Mar. 16	584.68	0.16	52.98	0.560	0.02	1.005	11.596
Mar. 17	584.68	0.16	53.10	0.560	0.02	1.009	11.571
Mar. 18	584.68	0.16	53.07	0.560	0.02	0.997	11.577

Number of readings, 10.
Time, 96 hours.
Osmotic pressure, 10.578.
Theoretical gas pressure, 10.213.
Ratio, 1.036.

Experiment No. 11—Temperature, 40°

Cell No. D_3. Manometer No. 39. Resistance of membrane, 80,000 ohms. Rotation of solution before experiment, 36°.6; after, 36°.6. Concentration of solution, 0.3 N. Cell set up April 21, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
Apr. 29	1050.64	0.17	127.02	0.513	0.02	0.995	8.805
Apr. 30	1050.64	0.17	126.87	0.513	0.02	0.990	8.813
May 1	1050.64	0.17	126.56	0.513	0.02	0.987	8.834
May 2	1050.64	0.17	127.17	0.513	0.02	0.991	8.795
May 3	1059.64	0.17	126.98	0.513	0.02	1.000	8.807
May 4	1050.64	0.17	127.89	0.513	0.02	1.005	8.814
May 5	1050.64	0.17	126.83	0.513	0.02	1.009	8.817

Number of readings, 9.
Time, 160 hours.
Osmotic pressure, 7.816.
Theoretical gas pressure, 7.660.
Ratio, 1.021.
This ratio was obtained with one of the new large-volume manometers.[1]

[1] See Carpenter's Dissertation, 1911.

Experiment No. 12—Temperature, 40°

Cell. No. I_5. Manometer No. 11. Resistance of membrane, 120,000 ohms. Rotation of solution before experiment, 24°.8; at conclusion, 24°.8. Concentration of solution, 0.2 N. Cell set up March 22, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
March 24	505.05	0.16	87.82	0.404	0.02	1.011	6.175
March 25	505.05	0.16	88.10	0.404	0.02	1.013	6.159
March 26	505.05	0.16	87.76	0.404	0.02	1.006	6.179
March 28	505.05	0.16	87.90	0.404	0.02	0.989	6.169
March 30	505.05	0.16	88.20	0.404	0.02	0.976	6.151
March 31	505.05	0.16	88.24	0.404	0.02	0.987	6.147
April 1	505.05	0.16	87.99	0.404	0.02	0.996	6.165

Number of readings, 10.
Time, 210 hours.
Osmotic pressure, 5.166.
Theoretical gas pressure, 5.106.
Ratio, 1.012.
On the 27th and 29th there were sudden increases of pressure, not caused by any change in temperature. It is seen that the cell had recovered in each case by the next day.

Experiment No. 13—Temperature, 40°

Cell No. P_3. Manometer No. 5. Resistance of membrane, 160,000 ohms. Rotation of solution before experiment, 24°.8; at conclusion, 24°.8. Concentration of solution, 0.2 N. Cell set up March 22, 1911.

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
April 8	505.05	0.16	103.03	0.465	0.02	0.999	6.159
April 9	505.05	0.16	102.99	0.465	0.02	1.009	6.163
April 10	505.05	0.16	102.66	0.465	0.02	1.014	6.180
April 11	505.05	0.16	102.74	0.465	0.02	1.014	6.176
April 12	505.05	0.16	102.87	0.465	0.02	1.018	6.168
April 13	505.05	0.16	102.94	0.465	0.02	1.015	6.165

Number of observations, 14.
Time, 120 hours.
Osmotic pressure, 5.158.
Theoretical gas pressure, 5.106.
Ratio, 1.010.

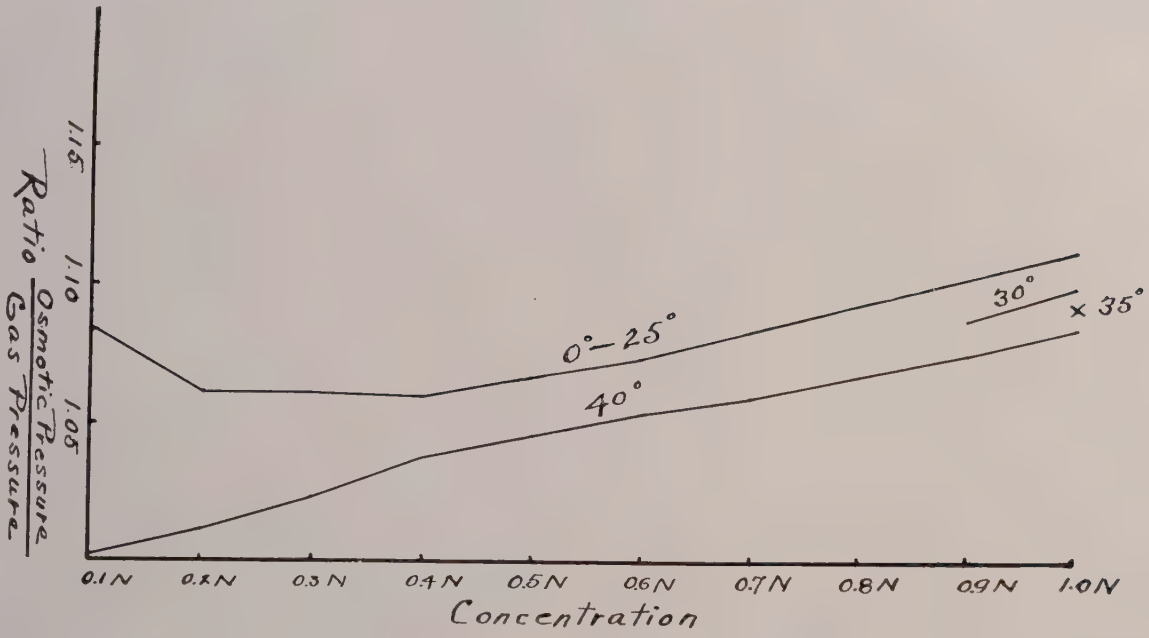
In this determination the initial pressure was about an atmosphere too high, and 17 days were required for equilibrium to be established. It would seem that some concentration should have been detected.

Experiment No. 14—Temperature, 40°

Cell No. F_3. Manometer No. 11. Resistance of membrane, 110,000 ohms. Rotation of solution at beginning of experiment, 12°.70; at conclusion, 12°.80. Concentration of solution, 0.1 N. Cell set up April 1, 1911, and was in the bath 51 days.

On April 3rd the ratio was 1.093
On April 6th the ratio was 1.064
On April 8th the ratio was 1.050
On April 11th the ratio was 1.042
On April 16th the ratio was 1.033
On April 20th the ratio was 1.021
On April 21st the ratio was 1.014
On April 26th the ratio was 1.001
On April 27th the ratio was 1.001
On April 28th the ratio was 1.002
On April 29th the ratio was 1.001
On April 30th the ratio was 1.007
On May 1st the ratio was 1.012
On May 2nd the ratio was 1.035
On May 3rd the ratio was 1.022
On May 4th the ratio was 1.015
On May 5th the ratio was 1.015
On May 6th the ratio was 1.016
On May 7th the ratio was 1.012
On May 8th the ratio was 1.012
On May 9th the ratio was 1.015
On May 10th the ratio was 1.011
On May 11th the ratio was 1.004
On May 12th the ratio was 1.002
On May 14th the ratio was 1.001
On May 15th the ratio was 1.004
On May 16th the ratio was 1.011
On May 17th the ratio was 1.008
On May 18th the ratio was 1.009
On May 19th the ratio was 1.004
On May 20th the ratio was 1.002
On May 21st the ratio was 0.999

This was one of the experiments in which there occurred a sudden increase of pressure that could hardly be explained by anything except a movement on the part of the closing mechanism. It will be observed that the initial pressure was rather high, but that this, in the course of 23 days, fell


Ratio Osmotic Pressure / Gas Pressure
1.15
1.10
1.05
0°–25°
30°
× 35°
40°
0.1N
0.2N
0.3N
0.4N
0.5N
0.6N
0.7N
0.8N
0.9N
1.0N
Concentration

off until the ratio was unity. The cell was an old and very slow one. This decrease in pressure was not regular. Between the 11th and the 16th it was fairly constant, and also between the 21st and 26th. On this day the ratio became unity, and remained so for 6 days. The figures on the 30th and 1st are high, but this was caused by a sudden and exceptionally low barometer, to which the cell was too slow to respond. On the 2nd the ratio jumps to 1.035, and then falls off again until unity is reached, where it remains, with one slight increase of pressure, for 11 days. The solution was found slightly concentrated and the ratios are corrected for this.

Summary

The measurements taken by Dr. Holland and Dr. Myers at 40° are as follows:

Mean of 3 on the 0.9 N solution	1.076
Mean of 3 on the 0.8 N solution	1.068
Mean of 3 on the 0.7 N solution	1.060
Mean of 2 on the 0.6 N solution	1.054
Mean of 2 on the 0.5 N solution	1.046
Mean of 2 on the 0.4 N solution	1.037
Mean of 3 on the 0.3 N solution	1.024
Mean of 3 on the 0.1 N solution	1.001

The mean by concentrations of all 32 determinations is tabulated below, and compared with the corresponding value for 0°–25°:

	0.1 N	0.2 N	0.3 N	0.4 N	0.5 N
40°	1.002	1.011	1.023	1.038	1.046
0°–25°	1.083	1.061	1.060	1.060	1.067

	0.6 N	0.7 N	0.8 N	0.9 N	1.0 N
40°	1.054	1.060	1.068	1.076	1.086
0°–25°	1.074	1.083	1.093	1.103	1.114

The marked deviation at 40° from the other values is shown strikingly by the curves. The ratios on the 1.0 N and 0.9 N solution at 30°, and the 1.0 N at 35°, are included.

Conclusions

The osmotic pressure of cane sugar solutions at 40° has been shown to depart in a marked manner from the values that have been obtained from 0° to 25°, and which have been the same for any given concentration through this range of temperature. *At 40° the ratios show a fairly regular increase with increase in concentration, beginning with a ratio of unity for the 0.1 N solution.* If hydration be the cause for the excess of osmotic over gas pressure, the hydrates are being broken down by the increase in temperature, and the apparently abnormal results that have been obtained between 0° and 25° are no longer so much in evidence. The curves indicate that as the temperature is increased the ratios of successively more and more concentrated solutions will become unity.

BIOGRAPHY

The writer was born at Sweetwater, Tennessee, November 19, 1886. He prepared for college at various schools in East Tennessee, and received the degree of A.B. from Emory and Henry in 1907. The following fall he entered Johns Hopkins Univeristy with Chemistry as major subject, Physical Chemistry and Mineralogy as minors. He was in charge of the Department of Chemistry of Emory and Henry College during the academic year 1909–'10.